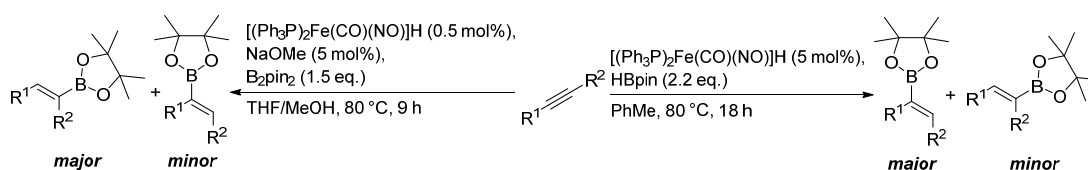


# IRON-CATALYSED HYDROBORATION OF UNSATURATED C-C BONDS: BORON-SOURCE CONTROLLED SELECTIVITY

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The well-defined iron-hydride complex  $[(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})(\text{NO})]\text{H}$  shows high activity in a manifold of catalytic reductions, such as the hydrosilylation of internal alkynes [1] or the hydrosilylation of carbonyl compounds and phosphine oxides.[2] To further explore the reactivity of this catalyst towards different classes of reductands, it was employed in the hydroboration of internal alkynes. After extensive optimisation of the reaction conditions, two protocols employing different boron sources were identified: either using *bis*(pinacolato)diboron ( $\text{B}_2\text{pin}_2$ ) or pinacolborane ( $\text{HBpin}$ ).[3]



Scheme 1: Switchable regioselectivity in the iron-catalysed hydroboration of internal alkynes.

With those two reaction conditions, a range of symmetrical and unsymmetrical internal alkynes was reacted to the corresponding vinylboronates in high (*Z*)/(*E*) selectivities and yields. For unsymmetrical internal alkynes, complementary regioselectivities were observed depending on the boron source used. To explain our findings, we propose a mechanistic dichotomy: borafermentation for  $\text{HBpin}$  and hydroferration for  $\text{B}_2\text{pin}_2$ .<sup>[3]</sup>

[1] C. Belger, B. Plietker, *Chem. Commun.* **2012**, 48, 5419. [2] S. Rommel, C. Belger, J.-M. Begouin, B. Plietker, *ChemCatChem* **2015**, 7, 1292. [3] F. Rami, B. Plietker, *manuscript submitted for publication*.